TRACE METAL AND NUTRIENT CYCLING IN SAN FRANCISCO BAY

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LONG TERM GOALS

The long term goals of this project are to examine the influence of metal flux (primarily Cu, Cd, Co, Mn and Fe) from sediments on the concentration of dissolved metals in the coastal zone and embayments. The processes that control trace metal exchange across the sediment-water interface within coastal environments regulate the concentration of dissolved, bioactive metals in the water column. These processes include variations in the relative influence of transport mechanisms (diffusion versus bio-irrigation), microbial activity (anaerobic versus aerobic respiration), as well as geochemical reactions (redox reactions, precipitation, complexation and adsorption) that regulate the behavior of dissolved metals in pore waters. All of these processes are controlled by the activity and composition of the sediment community. The role of organic carbon remineralization on trace metal mobility at a biologically active interface is, therefore, the focus of this study.

OBJECTIVES

Our long term objectives are to understand how sedimentary environments, which favor certain terminal electron acceptors (O_2, SO_4, Mn, Fe, etc...), affect the interaction between organic matter diagenesis and metal flux. Further, we must understand how the products and reactants of this diagenesis are transported between the sediments and the water column. In this study, measurements of carbon oxidation and metal flux are coupled with observations of dissolved metal concentrations in the water column to assess the strength of the sedimentary source. We have done this by coupling a study of organic matter diagenesis in sediments (W. Berelson, USC) with our measurement of metal flux across the sediment-water interface and vertical distribution of metals in sediment pore waters. We are extrapolating our study of the LA/Long Beach Harbor systems with a study of South San Francisco Bay.

In addition to the above long term objectives, the first year's task was to develop new deployment and instrumentation capabilities which would allow us to 1) deploy and recover landers from a small boat allowing us more access to shallow sites, 2) determine the change in chemical concentrations within the chambers in high resolution, 3) core the sediments directly beneath the chamber to understand more about the mechanism of solute transport.

APPROACH

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Our approach was to measure directly, the benthic fluxes of trace metals (Cd, Mn, Co, Cu and Fe) and nutrients (oxygen, nitrate, ammonia, phosphate, silicate, TCO_2, alkalinity and ^{222}Rn) from sediments within San Francisco Bay utilizing benthic chambers. The depth distribution of these chemicals in the sediment was also to be determined in cores collected at the same sites where fluxes were measured. Our previous work has used benthic flux chambers designed for deep-sea deployments. In 1996, together with W. Berelson at USC, we developed a sea-floor incubation chamber that can be used more readily for environmental manipulation experiments in shallow systems. All of these measurements are accompanied by observations of dissolved metal concentrations in the water column. We have worked to develop an *in situ* chemical analyzer based on new digital pump technology, which is capable of conducting colorimetric analyses of both chamber and ambient waters. We have applied a stoichiometric approach to identify the importance of terminal electron acceptors and anoxic diagenesis in carbon remineralization, nutrient and metal release.

Our approach is to couple manipulative experiments of macrofaunal and microbial communities to assess their role in mediating chemical transport. The new chamber design allows for a variety of *in situ* operations. Manipulations involve the injection of oxygen (to assess the role of bottom water oxygen concentrations), acid (to determine the effects of changing pH), formaldehyde (to provide a diffusional control), molybdate (to quantify the role of sulfate reducing bacteria) and the injection of fluorescent latex beads in untreated chambers and chambers treated with formalin (to obtain preliminary measurements of biologically mediated particle removal mechanisms).

WORK COMPLETED

In continuation of our LA/Long Beach Harbor Processes Studies, we have initiated our field efforts, now in San Francisco Bay. Our second field effort there, following a period of instrumental development, was highly successful on several fronts. Modification of our 22 foot Boston Whaler now allows for the deployment and recovery of two fully equipped divers and benthic flux chambers. The new benthic flux chamber, built by Will Berelson, functioned flawlessly and has been reconfigured to allow a wide variety of benthic manipulative experiments. These experiments include 1) the opening and closing of chamber ports to allow for sequential measurements of flux without altering bottom water oxygen or pH significantly, 2) the injection of fluorescent beads to trace POC removal processes, and 3) the injection of CsBr to monitor rates of bioirrigation. In addition, we have accessorized the benthic flux chamber with a new evolution of the *in situ* chemical analyzer (The Digital Scanner), now enabling us to perform *in situ* spectrophotometric analyses of chamber waters, and a coring device (The Intrudinator) which can be programmed to take and return intact sediment cores from within the chamber area. The Digital Scanner was configured to determine nitrate within chamber waters and the Intrudinator successfully returned cores for pore water analysis on every deployment. The benthic flux chamber we have developed is now much more than a simple 'bell-jar' apparatus for conducting solute flux measurements. The new capabilities of our chamber allow us to conduct coupled studies of particulate and solute cycling. The use of a benthic chamber for this purpose is necessary for work in coastal bays and harbors because sediment benthos play such an important role in sediment diagenesis.

This year we have deployed and recovered benthic chambers during two seasons and at 5 sites in San Francisco Bay, retrieved, sectioned and extracted pore waters from 6 cores and measured the concentrations of most of the trace metals of interest in all of these samples.

RESULTS

Preliminary results from comparisons of both new and old style chambers indicate that both produce the same results. Although some of the samples from the last field effort have yet to be analyzed, these results together with those of the LA/Long Beach Harbors, demonstrate the importance of dissolved metal fluxes from sediments in regulating the concentration of dissolved, bioactive metals in the system. For instance, the major source of dissolved cadmium is flux from undisturbed sediments which are low in organic carbon content as cadmium appears to be trapped in sediments in which sulfide is produced. Many sites within the LA\Long Beach system have cadmium fluxes which are into the sediments.

The results of the manipulative experiments demonstrate the importance of understanding the processes that control flux. Injecting metabolic inhibitors causes a dramatic decreases in metal flux, which indicates the importance of microbial remineralization in regulating metal flux. However, organic carbon remineralization alone is not the most important factor in regulating flux.

IMPACT

Our results will directly impact the consideration of sediment decontamination measures. We have identified the sediments as sources for some metals and a sink for others, the sign depends upon the macrofauna and microbial activity. Although this is a more complicated picture, it has the potential to be exploited selectively where mobilization or preservation of a particular contaminant is desired. In this new environment, with these new capabilities, we are now in a position to perform some very novel experiments. For example, San Francisco Bay has been infested with the Asian Clam (*Potamocorbula amurensis*). This voracious filter feeder made its way here in the ballast of ships in 1984 and now controls the blooms of phytoplankton in the Bay. There is some emerging evidence that it may also play a role in mercury cycling as well. We have been engaged in discussions with researchers from USGS who are well acquainted with the biology of this organism, but we believe there is an important geochemical side to this story as well. We believe that the Asian clam plays an important role in actively transporting particulate organic carbon (and elements adsorbed to these particles) from the water column to the sediments, thereby affecting not only the rate of POC transport, but the diagenetic environment downcore, and the resultant flux of dissolved constituents (trace metals and nutrients) from the sediments. For example, anaerobic sediments, rich in organic carbon, favor the methylation of mercury, methyl mercury can be accumulated in clam tissue and bio-amplified up the food chain. This is but one organism that may serve to mediate the transport of materials from the water column to the sediments and back. Other macrofaunal invertebrates, many of which are also invasive species, also function as the gatekeepers of transport.

This project has significant impacts for our understanding of the behavior of metals in coastal systems. In particular, it supplies important baseline information to assess the environmental consequences of dredging (removes dissolved Cd), remediation and eutrophication. It allows us to separate the natural and anthropogenic processes that both lead to elevated metal concentrations in embayments. New studies with benthic macrofauna will allow for emerging hypotheses of metal accumulation and transport to be directly assessed with environmental measurements under relevant flow conditions.

TRANSITIONS

As we move our research from low energy boundary layers into high energy boundary layers, both the role of macrofauna become more pronounced and reproduction of the hydrodynamic regime becomes more important. In the deep-sea, passive particle settling determines POC delivery to the sediments. In areas heavily populated by macrofauna, their behavior also plays a major role in POC flux. Whereas the current stirring bars within the chambers reproduce the boundary layer of the deep-sea environment, there is some evidence to suggest that the advective conditions of the environment, within the chamber, is an important factor which may regulate the rate at which macrofauna filter-feed/bioirrigate, and thus move both solute and particulate phase materials between the water column and underlying sediments.

RELATED PROJECTS

Both the California Department of Fish and Game (CDFG) and the United States Geological Survey/Water Resources Division (USGS/WRD) have keen interest in the cycling of contaminant metals and the role of benthic macrofauna in the Bay (especially the invasive species such as *Potamocorbula*) but have no direct way to assess the flux of these contaminants between the water column and the sediments. Our measurements will compliment the studies being undertaken by these agencies. We have collected samples of pore waters for Dr. James Kuwabara (USGS/WRD) for the analysis of acid volatile sulfur species (AVS). AVS has been shown to be a proxy for excess metal binding potential of pore waters and an indicator of toxicity. We intend to correlate these measurements with those of metal flux and metal porewater profiles in the interpretation of our results. We have initiated a study of the potential role of benthic macrofauna in collaboration with Dr. Jan Thompson (USGS/WRD) and are working with her to improve the chamber design as pertaining to the boundary layer. Mark Stephenson (CDFG) has expressed interest in collaborating with us on some measurements of mercury cycling at the sediment/seawater boundary. We have discussed the design of some experiments in which mercury injected into chambers could be traced through the sediments, macrofauna and back into the water column as a methylated species. We have been funded by NSF to develop new methodologies for *in situ* chemical analyses, using the Digital Scanner and will incorporate this technology into our study of chemical fluxes in San Francisco Bay. Lastly, we have submitted an ASSERT proposal to fund a graduate student who will work closely with us, the USGS and the CDFG on these collaborative projects. Her emphasis will be on the role of benthic macrofauna as the gatekeepers of material transport (POC, trace metals and nutrients) between the water column and the sediments. She will characterize our deployment sites with respect to macrofauna biomass and behavior (filter feeding, surface feeding or burrowing) and relate these findings to trace metal flux, particle removal, depth and rate of tracer transport.